

Supporting Information
for
Solid Effect in Magic Angle Spinning
Dynamic Nuclear Polarization

Björn Corzilius, Albert A. Smith, and Robert G. Griffin

Francis Bitter Magnet Laboratory and Department of Chemistry

Massachusetts Institute of Technology

77 Massachusetts Avenue

Cambridge, MA 02139, USA

Derivation of DNP parameters for the zero quantum (ZQ) case

Here we derive the rate equations describing the excitation of the ZQ electron-nuclear coherence. A similar treatment for the DQ case has been demonstrated in the main text. We begin with the complete electron-nuclear spin Hamiltonian including the microwave induced coupling terms in the eigenframe of the static Hamiltonian, in the form given in eqn. (24):

$$\begin{aligned} H' = & \frac{1}{2} \left[(\Delta\omega_{0S} - \omega_{0I})(S_z + I_z) + A(S_z + I_z)I_z - \frac{\omega_{1S}B}{2\omega_{0I}}(S^+I^+ + S^-I^-) \right] \\ & + \frac{1}{2} \left[(\Delta\omega_{0S} + \omega_{0I})(S_z - I_z) + A(S_z - I_z)I_z + \frac{\omega_{1S}B}{2\omega_{0I}}(S^+I^- + S^-I^+) \right]. \quad (S1) \\ & + \frac{\omega_{1S}}{2}(S^+ + S^-) \end{aligned}$$

We now select the ZQ subspace (line 2 in (S1)) while neglecting the DQ subspace and the SQ coherences for the same arguments made in the main text. The separated ZQ subspace has the form:

$$H'_{\text{ZQ}} = \frac{1}{2} \left[\Omega_{\text{DNP}}^{\text{ZQ}} (S_z - I_z) + A(S_z - I_z)I_z + \frac{\omega_{1S}B}{2\omega_{0I}} (S^+I^- + S^-I^+) \right] \quad (\text{S2})$$

In (S2) we have introduced $\Omega_{\text{DNP}}^{\text{ZQ}} = \Delta\omega_{0S} + \omega_{0I}$ as the offset between the microwave frequency and the ZQ matching condition. Furthermore, we can drop the secular part of the electron-nuclear coupling term, since within this subspace the corresponding operator takes the form of an identity matrix and only leads to an offset of the eigenstates in the ZQ subspace with respect to the DQ subspace. We are left with a truncated ZQ Hamiltonian of the form

$$H'_{\text{ZQ}}^{(0)} = \frac{1}{2} \left[\Omega_{\text{DNP}}^{\text{ZQ}} (S_z - I_z) + \frac{\omega_{1S}B}{2\omega_{0I}} (S^+I^- + S^-I^+) \right]. \quad (\text{S3})$$

If we consider this Hamiltonian in the DQ subspace (as depicted in Fig. 2), we see that it resembles a simple one-spin Hamiltonian consisting of a Zeeman term and a coupling term, driven by microwave irradiation. Accordingly, we can redefine a basis set for this subspace, which resembles the basis set of a single-spin in Hilbert-space. This basis set (incl. the respective raising and lowering operators) is given in Table I. We see that if the ZQ matching condition is fulfilled, magnetization stored in $\langle S_z - I_z \rangle / 2$ (corresponding to $\langle \sigma_z \rangle$ in the single spin case) is transformed into $\langle S^+I^- - S^-I^+ \rangle / 2i$ (corresponding to $\langle \sigma_y \rangle$) under influence of the microwave term $(S^+I^- + S^-I^+) / 2$ (corresponding to σ_x). $\langle S^+I^- - S^-I^+ \rangle / 2i$ magnetization will further evolve to $-\langle S_z - I_z \rangle / 2$ and subsequently to $-\langle S^+I^- - S^-I^+ \rangle / 2i$, and will finally return to $\langle S_z - I_z \rangle / 2$. If the microwave frequency is applied with an offset to the actual ZQ matching

condition, magnetization in $\langle S^+I^- - S^-I^+ \rangle / 2i$ will be in parallel evolving into $\langle S^+I^- + S^-I^+ \rangle / 2$ and then into $-\langle S^+I^- - S^-I^+ \rangle / 2i$, from where the microwave field will drive it back to $\langle S_z - I_z \rangle / 2$; note that the return to $\langle S_z - I_z \rangle / 2$ results in a reduction of the SE transfer efficiency. So we see that this spin system can be described by the common Bloch equations in analogy to a single spin system.

To do so, we define the following set of expectation values that fulfill the usual commutation relations:

$$\begin{aligned}
P_S &= M_{S_z} = \langle S_z \rangle \\
P_I &= M_{I_z} = \langle I_z \rangle \\
M_x &= \langle S^+I^- + S^-I^+ \rangle / 2 \\
M_y &= \langle S^+I^- - S^-I^+ \rangle / 2i
\end{aligned} \tag{S4}$$

where P_S and P_I are the polarization of the electrons and nuclear spins respectively, and M_x and M_y are the transverse ZQ coherences. Now we can define a set of differential equations which describe magnetization kinetics for the ZQ case:

$$\begin{aligned}
\frac{dP_S}{dt} &= -\omega_{\text{DNP}} M_y + \frac{1}{T_{1S}} (P_{S,\text{eq}} - P_S) \\
\frac{dP_I}{dt} &= -\omega_{\text{DNP}} M_y + \frac{1}{T_{1I}} (P_{I,\text{eq}} - P_I) \\
\frac{dM_x}{dt} &= -\Omega_{\text{DNP}} M_y - \frac{1}{T_{2,\text{DNP}}} M_x \\
\frac{dM_y}{dt} &= \omega_{\text{DNP}} \frac{(P_S + P_I)}{2} + \Omega_{\text{DNP}} M_x - \frac{1}{T_{2,\text{DNP}}} M_y
\end{aligned} \tag{S5}$$

In this case Ω_{DNP} is the offset between the mw frequency and the ZQ transition frequency.

Under the assumption of quasi-equilibrium (see main text) we find

$$M_x = -\Omega_{\text{DNP}} T_{2,\text{DNP}} M_y. \tag{S6}$$

Inserting (S6) into (S5) yields

$$M_y = \frac{\omega_{\text{DNP}} T_{2,\text{DNP}}}{1 + (\Omega_{\text{DNP}} T_{2,\text{DNP}})^2} \frac{(P_S + P_I)}{2}, \quad (\text{S7})$$

which in turn can be inserted into (S5), giving us effective terms describing the buildup and decay of electron and nuclear polarization during microwave irradiation of the solid effect transition:

$$\begin{aligned} \frac{dP_S}{dt} &= -\frac{\omega_{\text{DNP}}^2 T_{2,\text{DNP}}}{2(1 + (\Omega_{\text{DNP}} T_{2,\text{DNP}})^2)} (P_S + P_I) + \frac{1}{T_{1S}} (P_{S,\text{eq}} - P_S) \\ \frac{dP_I}{dt} &= -\frac{\omega_{\text{DNP}}^2 T_{2,\text{DNP}}}{2(1 + (\Omega_{\text{DNP}} T_{2,\text{DNP}})^2)} (P_S + P_I) + \frac{1}{T_{1I}} (P_{I,\text{eq}} - P_I) \end{aligned} \quad (\text{S8})$$

Defining the rate constant

$$k_{\text{DNP}} = \frac{\omega_{\text{DNP}}^2 T_{2,\text{DNP}}}{2(1 + (\Omega_{\text{DNP}} T_{2,\text{DNP}})^2)} \quad (\text{S9})$$

yields

$$\begin{aligned} \frac{dP_S}{dt} &= -k_{\text{DNP}} (P_S + P_I) + \frac{1}{T_{1S}} (P_{S,\text{eq}} - P_S) \\ \frac{dP_I}{dt} &= -k_{\text{DNP}} (P_S + P_I) + \frac{1}{T_{1I}} (P_{I,\text{eq}} - P_I) \end{aligned} \quad (\text{S10})$$

These rate equations only describe a pair of one electron and one nuclear spin. If one electron spin polarizes several nuclear spins we have to generalize (S10) to:

$$\begin{aligned} \frac{dP_S}{dt} &= -\sum_{m=1}^{N_I} k_{\text{DNP}}^m (P_S + P_I^m) + \frac{1}{T_{1S}} (P_{S,\text{eq}} - P_S) \\ \frac{dP_{I,m}}{dt} &= -k_{\text{DNP}}^m (P_S + P_I^m) + \frac{1}{T_{1I}^m} (P_{I,\text{eq}}^m - P_I^m) \end{aligned} \quad (\text{S11})$$

If we now assume that spin-diffusion leads to a fast equilibration of all nuclei, we see that

$$\begin{aligned}\frac{dP_S}{dt} &= -\frac{N_I}{N_S} k_{\text{DNP}} (P_S + P_I) + \frac{1}{T_{1S}} (P_{S,\text{eq}} - P_S) \\ \frac{dP_I}{dt} &= -k_{\text{DNP}} (P_S + P_I) + \frac{1}{T_{1I}} (P_{I,\text{eq}} - P_I)\end{aligned}\quad (\text{S12})$$

Note that we have dropped all indices m because all nuclei are now indistinguishable.

During DNP, polarization will build up in the pool of nuclear spins and will eventually reach a steady state polarization when

$$\frac{dP_I}{dt} = -k_{\text{DNP}} (P_S^\infty + P_I^\infty) + \frac{1}{T_{1I}} (P_{I,\text{eq}} - P_I^\infty) = 0. \quad (\text{S13})$$

P_S^∞ and P_I^∞ describe the electron and nuclear polarization in the steady state, respectively. We now introduce the DNP enhancement factor at infinite polarization time:

$$\varepsilon_\infty = \frac{P_I^\infty}{P_{I,\text{eq}}}, \quad (\text{S14})$$

so we can now rearrange (S13) to obtain

$$k_{\text{DNP}} \left(\frac{P_S^\infty}{P_{I,\text{eq}}} + \varepsilon_\infty \right) = -\frac{1}{T_{1I}} (\varepsilon_\infty - 1). \quad (\text{S15})$$

This allows us to calculate our enhancement, if the DNP rate constant, nuclear longitudinal relaxation time and the steady-state electron spin polarization are known:

$$\varepsilon_\infty = \frac{1 - k_{\text{DNP}} T_{1I} \frac{P_S^\infty}{P_{I,\text{eq}}}}{1 + k_{\text{DNP}} T_{1I}} = \frac{1 - K_{\text{DNP}} \frac{P_S^\infty}{P_{I,\text{eq}}}}{1 + K_{\text{DNP}}} \quad (\text{S16})$$

Here, $K_{\text{DNP}} = k_{\text{DNP}} T_{1I}$ has been introduced, which can be considered as an effective DNP equilibrium constant between DNP buildup and polarization decay by longitudinal nuclear spin relaxation. If the steady-state enhancement and the steady-state electron polarization are known, K_{DNP} can be calculated by:

$$K_{\text{DNP}} = k_{\text{DNP}} T_{1l} = -\frac{(\varepsilon_{\infty} - 1)}{\left(\frac{P_S^{\infty}}{P_{l,\text{eq}}} + \varepsilon_{\infty}\right)}. \quad (\text{S17})$$